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Yangang Ren [1], Max R. McGillen [1,2], Véronique Daële [1], Jérôme Casas [3], Abdelwahid Mellouki [1]*

Affiliations

1. Institut de Combustion Aérothermique, Réactivité et Environnement, Centre National de la Recherche Scientifique (ICARE-CNRS), Observatoire des Sciences de l'Univers en région Centre (OSUC), CS 50060, 45071 cedex02, Orléans, France
2. Le Studium Loire Valley Institute for Advanced Studies, Orléans 45071, France
3. Institut de Recherche sur la Biologie de l'Insecte, UMR 7261, Université de Tours, 37200, Tours, France

Corresponding author

* mellouki@cnrs-orleans.fr

Abstract

Phytohormones emitted into the atmosphere perform many functions relating to the defence, pollination and competitiveness of plants. To be effective, their atmospheric lifetimes must be sufficient that these signals can be delivered to their numerous recipients.

We investigate the atmospheric loss processes for methyl salicylate (MeSA), a widely emitted plant volatile. Simulation chambers were used to determine gas-phase reaction rates with OH, NO_3, Cl and O_3; photolysis rates; and deposition rates of gas-phase MeSA onto organic aerosols. Room temperature rate coefficients are determined (in units of cm^3 $molecule^{-1}$ s^{-1}) to be $(3.20\pm0.46)\times10^{-12}$, $(4.19\pm0.92)\times10^{-15}$, $(1.65\pm0.44)\times10^{-12}$ and $(3.33\pm2.01)\times10^{-19}$ for the reactions with OH, NO_3, Cl and O_3 respectively. Photolysis is negligible in the actinic range, despite having a large reported near-UV chromophore. Conversely, aerosol uptake can be competitive with oxidation under humid conditions, suggesting that this compound has a high affinity for hydrated surfaces. A total lifetime of gas-phase MeSA of 1–4 days was estimated based on all these loss processes.

The competing sinks of MeSA demonstrate the need to assess lifetimes of semiochemicals holistically, and we gain understanding of how atmospheric sinks influence natural communication channels within complex multitrophic interactions. This approach can be extended to other compounds that play vital roles in ecosystems, such as insect pheromones, which may be similarly affected during atmospheric transport.

Keywords: methyl salicylate (MeSA), atmospheric chemistry, kinetics, simulation chamber, odor aerosol transport, multitrophic interactions, phytohormones

1. Introduction

The emission of biogenic volatile compounds (BVOCs) into the atmosphere by vegetation carries a metabolic cost, but also concomitant benefits. Methyl salicylate (MeSA, methyl 2-hydroxybenzoate) is an example of a phytohormone that is emitted from a broad variety of species. For example, in their review on floral scents, Knudsen et al. (2006) listed 51 families of flowering plants that have been identified as MeSA emitters in the literature, encompassing many of the world's most economically important crops (such as apples, peaches, almonds and strawberries) in addition to many of the floral constituents of natural ecosystems. There are several proposed strategies by which plants can be advantaged through MeSA emission, as defence mechanisms, as an attractant for pollinators and as a method for reducing the local density of competing plants. MeSA has been observed to be involved in the following interactions:

1. Plant-herbivore interactions: MeSA can stimulate systemic acquired resistance (SAR) responses in healthy plant tissues (Park et al., 2007). This triggers salicylic acid production in the heathy tissues of a plant or in neighbouring plants, which primes plant defences against future herbivorous attacks (Thulke and Conrath, 1998). Furthermore, MeSA may act as a repellent towards certain herbivores (Hardie et al., 1994), although it may be difficult to decouple this effect from other deterrents such as SAR.

2. Plant-predator interactions: Several beneficial arthropods, that are known to predate upon herbivorous pests have been found to use the MeSA emissions of herbivore-infested plants in locating their prey (De Boer and Dicke, 2004; James, 2003; James and Price, 2004), thus reducing herbivorous attacks indirectly.

3. Plant-pollinator interactions: MeSA is a common floral scent that can attract pollinating insects (Dudareva et al., 1998; Knudsen et al., 2006; Loughrin et al., 1991), and is therefore an important component of the reproductive cycle in many flowering plants.

4. Plant-plant interactions: MeSA has been found to exhibit allelopathic effects (Bi et al., 2007), which may interfere with other species growth processes and reduce the root growth of neighbouring plants, favouring the emitter in a competition for soil nutrients.

For each of these four strategies, there is an apparent target for the MeSA emission, and efficient transport between the emitter and the recipient is required in order for these signalling chemicals to perform their function, particularly for cases where transport over long distances is necessary. It is therefore logical that the atmospheric lifetime of MeSA is sufficiently long that transport can occur prior to any chemical transformation in the atmosphere.

Enhanced emissions of MeSA may also occur as a consequence of biotic stress factors such as pathogen infection (Jansen et al., 2011; Martini et al., 2016), or abiotic stresses such as wounding, drought, temperature changes or ozone exposure (Chalal et al., 2015; Heiden et al., 1999; Karl et al., 2008). In these cases, there may be no obvious target for the emission of MeSA and this may be an immune response of wounded or diseased plants. Under these circumstances, MeSA emissions can represent a large flux, which can be comparable or even exceed that of monoterpenes (Karl et al., 2008). If these emissions are a response to abiotic stress factors such as drought or temperature swings, then these fluxes could be occurring across the scale of an ecosystem, which, depending on the atmospheric chemistry of MeSA, could have a major impact upon regional air quality.

Besides the biogenic emissions, which are expected to represent the dominant fluxes of MeSA into the atmosphere, several anthropogenic sources of MeSA exist, which could come from washing and cleaning products, disinfectants, air fresheners, polishes, waxes, cosmetics, personal care products and perfumes (European Chemicals Agency, 2020). Such emissions could impact indoor air quality, and knowledge of the oxidation reactions of MeSA is therefore important in assessing this.

The aim of this work is therefore to assess the various ways in which MeSA can interact with the atmospheric environment, which will allow a first assessment of the sensitivity of MeSA as a

phytohormonal signal towards transport in the atmosphere. Furthermore, these data will provide insight into the role that a large MeSA emission could play in regional air pollution.

2. Experimental methods

2.1 Chamber systems:

Two simulation chamber systems were employed in this work. For particle uptake experiments, the HELIOS chamber was used, which has been described elsewhere (Ren et al., 2019, 2017). In brief, HELIOS is a 90 m^3 hemispherical FEP Teflon foil chamber equipped with two Teflon fans installed at the base, which generate flow velocities of 14 m s^{-1} and induce rapid mixing of reactants in approximately 90 seconds. A three-axis ultrasonic anemometer (Delta Ohm, HD 2003) installed in the centre of the chamber was used to determine pressure, temperature and wind speed/ direction. Relative humidity (RH) was controlled using a water spray system, and was monitored using a humidity probe (Vaisala, HMT333). The chamber was cleaned overnight after each experiment with a fast flow (800 L min^{-1}) of zero air supplied by a pure air generation system (AADCO Instruments, Inc., 737 series).

Kinetic and photolysis measurements were conducted in the 7.3 m^3 ICARE-CNRS chamber, described previously (Bernard et al., 2010). This is a FEP Teflon foil chamber of a cuboidal design, equipped with Teflon fans that promote mixing within 1–2 mins. Illumination was provided artificially from lamp output centred at 254 nm (14 × UV-C T-40 L, Viber Lourmat); at 365 nm (24 × UV-A T-40 L, Viber Lourmat); and broad emissions, >300 nm, from sunlight simulating lamps (12 × Ultra-Vitalux 300 W, Osram). A thermocouple (PT-100) and a humidity probe (Vaisala HMT330) measured the temperature and RH.

Both chambers were operated at a slight overpressure to compensate for sample flows and small leaks, which was achieved using a continuous flow of zero air (5–60 L min^{-1}). This led to gradual dilution of the chamber contents. This was quantified using SF_6 as a tracer, which was monitored

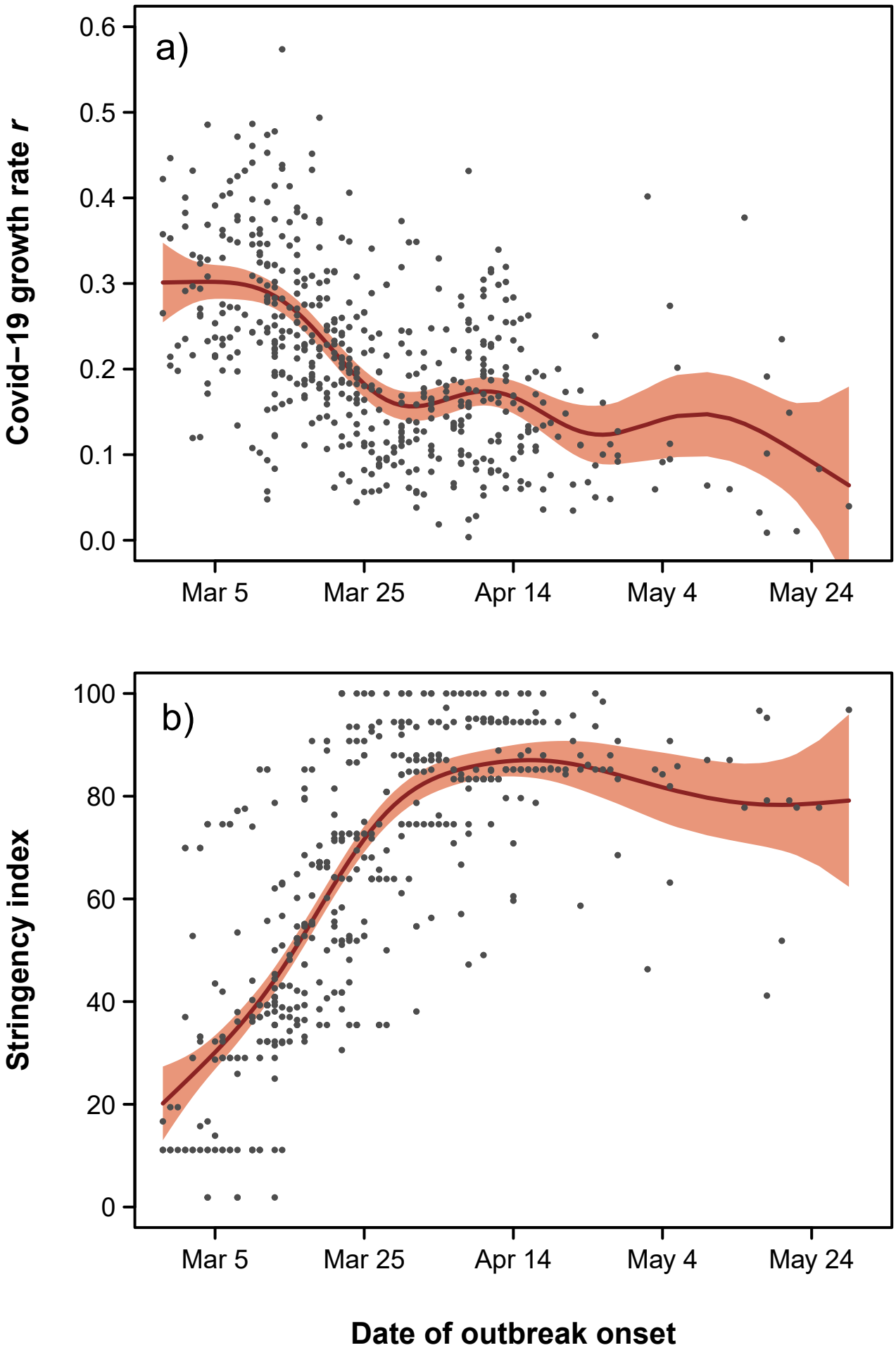
throughout the experiments using Bruker Vertex 70 (pathlength: 303 m) and Nicolet 5700 Magna (pathlength: 143 m) Fourier-transform infrared spectrometers coupled with white-type multipass optics for HELIOS and the 7.3 m^3 chamber respectively.

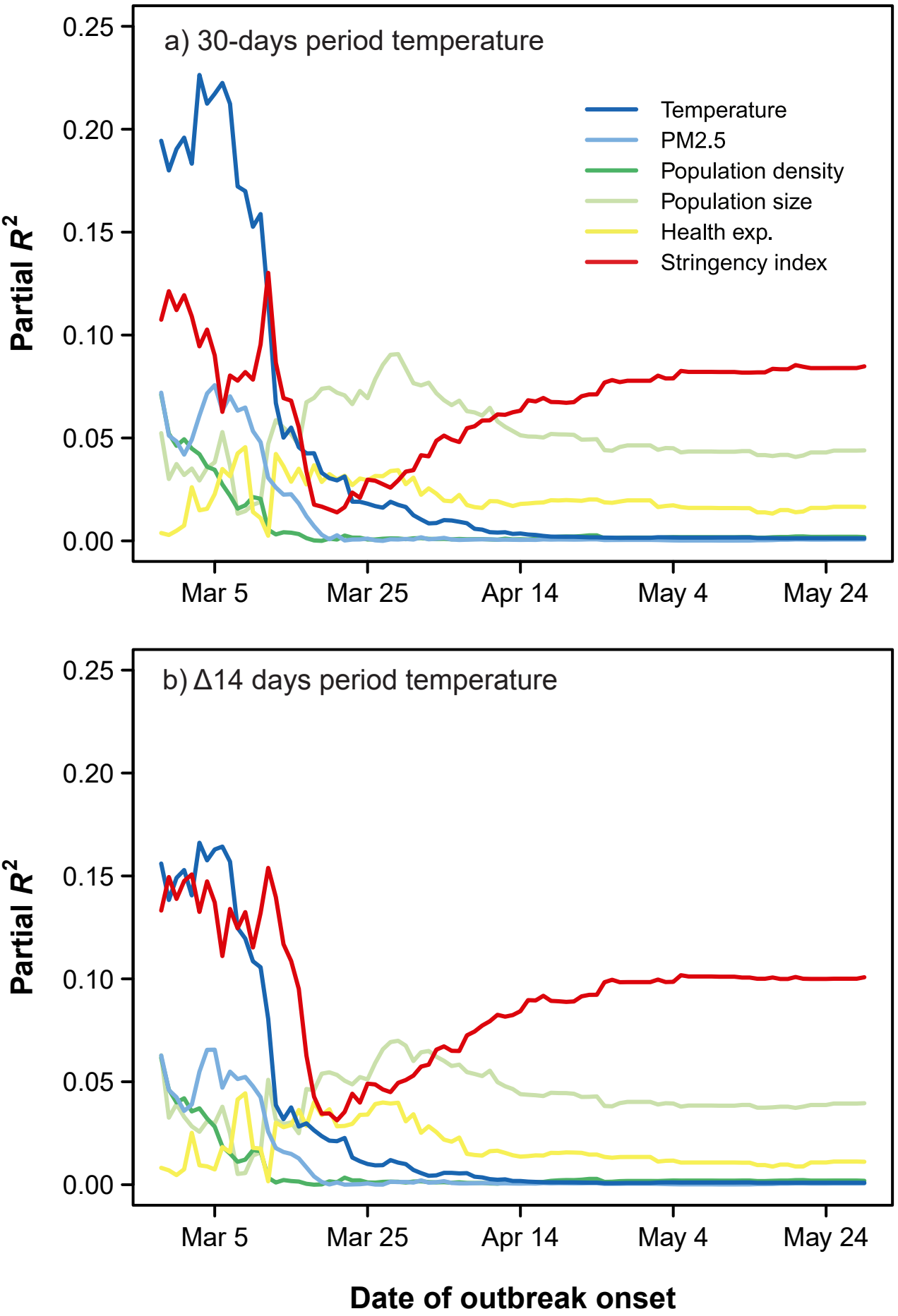
2.2 Organic compound analysis in the gas and particle phases, and aerosol measurements:

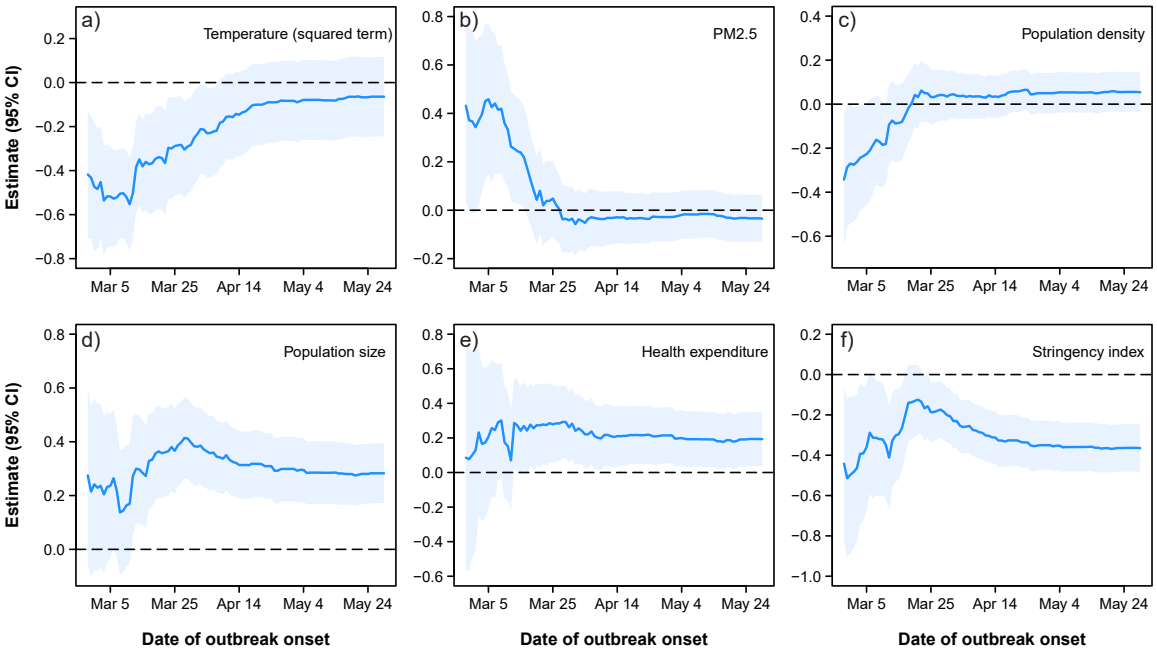
Gas-phase MeSA together with several other organic compounds were monitored using a high-resolution proton transfer reaction time-of-flight mass spectrometer (Ionicon Analytik, PTR-ToF-MS 8000) with a hydronium ion (H_3O^+) detection scheme. The pressure and voltage in the PTR-ToF-MS drift tube was maintained at 2.4 mbar and 480 V affording an electric field strength of 99 Td. The sampling flow was 0.1 L min^{-1}, through a 1 m long, ⅛ inch OD PEEK tube heated to 333 K. A high-resolution time-of-flight FIGAERO-ToF-CIMS instrument (Aerodyne Research Inc. and Tofwerk) with an I^- ionization scheme, similar to instruments described elsewhere (Lee et al., 2014; Lopez-Hilfiker et al., 2014), was used to determine concentrations of MeSA in the gas and particle phases. Voltages affecting ion transmission and declustering were optimized to maximize MeSA.I^- signal using the Thuner software (Tofwerk). The sampling protocol was as follows: aerosol samples were collected through a 1 m long, ¼ inch OD straight length of stainless steel tube at a flow rate of 2 L min^{-1} onto a PTFE filter (SKC, Zefluor™ 25 mm, 2 µm) for 20 mins, and were volatilized by slowly ramping the temperature of a 2 L min^{-1} carrier flow of N_2 from 298 to 573 K over 30 mins, which was held at 573 K for 20 mins subsequently, to ensure that the all particulate-phase MeSA had been thoroughly desorbed. Gas-phase samples were taken during the aerosol collection phase, through a 1 m long, ¼ inch OD PFA tube, also at a flow of 2 SLM. Aerosol size distributions were monitored using a single mobility particle sizer and differential mobility analyzer (3080, 3081 and 3085, TSI) coupled with a condensation particle counter (3788, TSI).

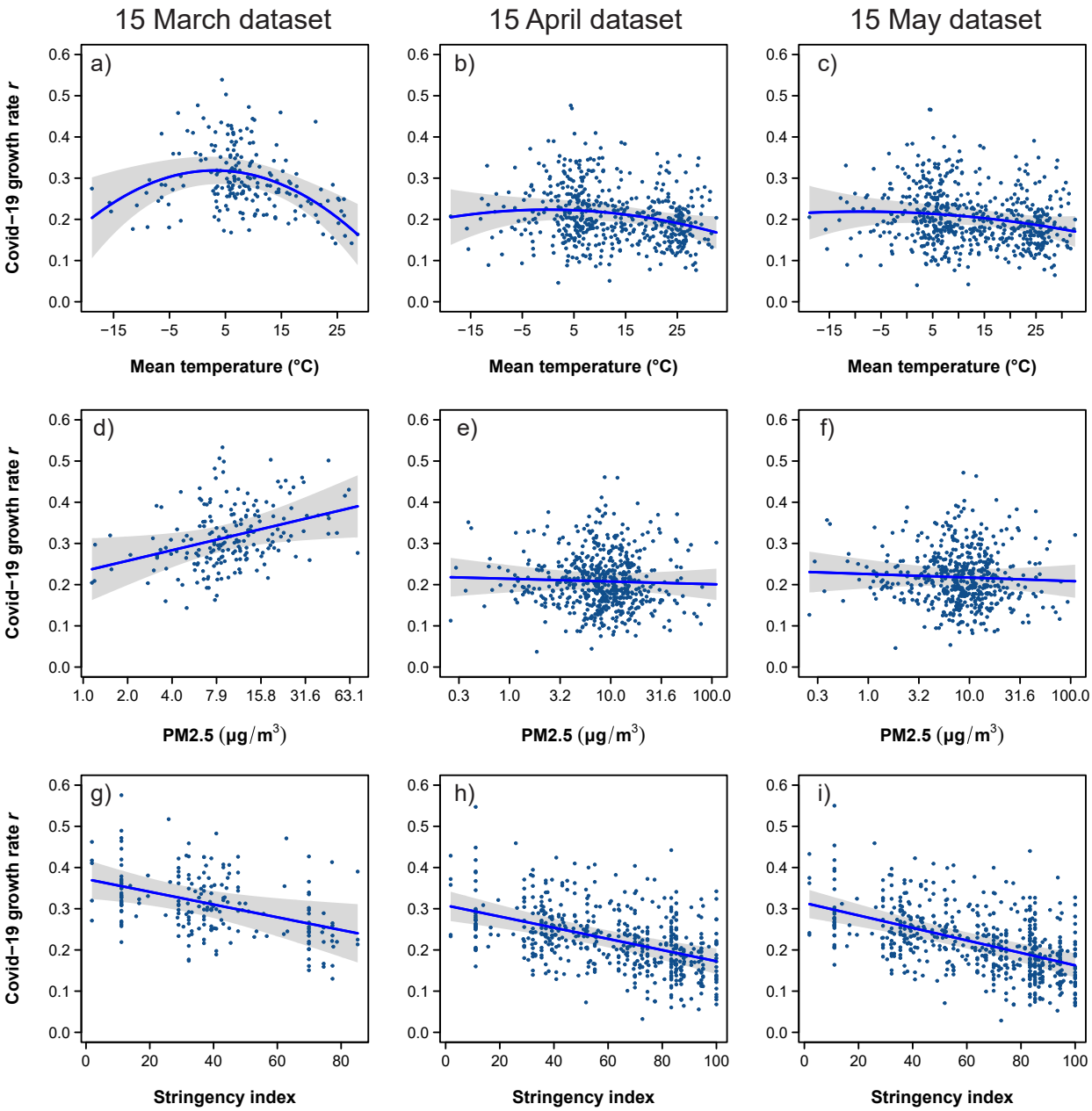
2.3 MeSA introduction system:

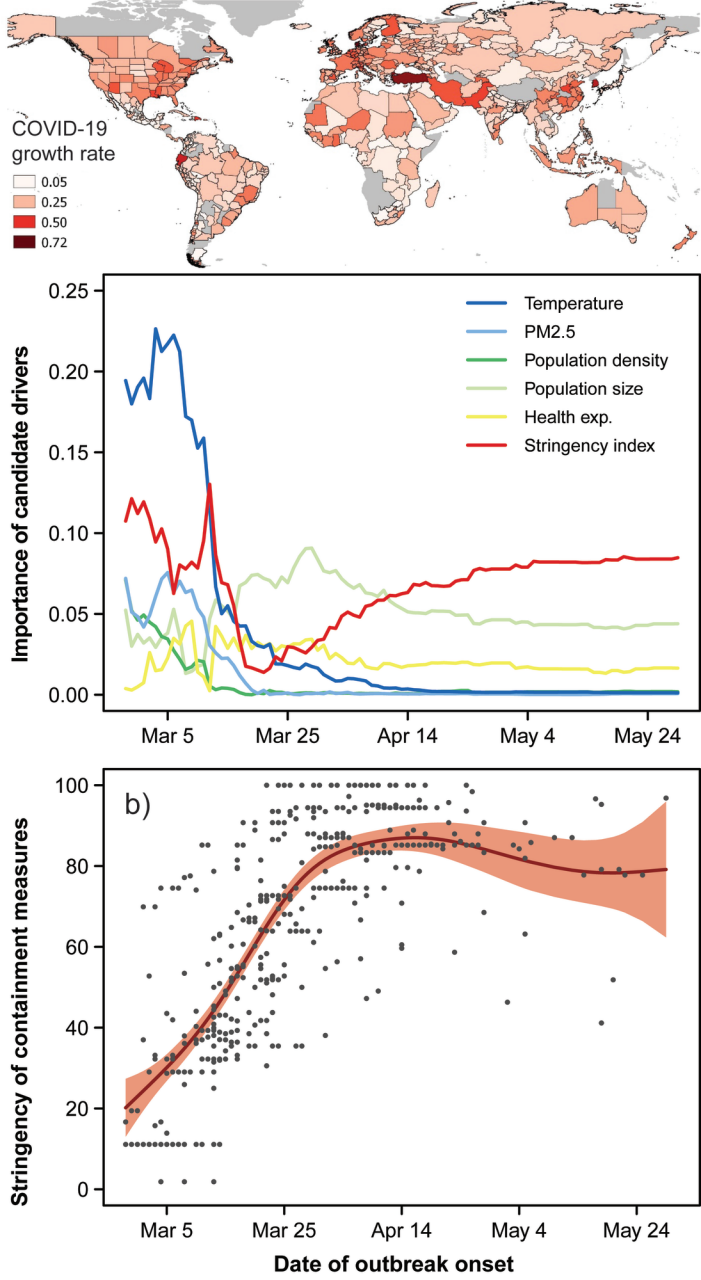
Because of the low vapor pressure of MeSA, 0.086 Torr at 298 K (Yaws, 2015), it is difficult to introduce into the chamber using the conventional method of impinging a liquid sample into a


a)
Covid−19 growth rate r
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Mar 5
Mar 25
Apr 14
May 4
May 24
b)
Stringency index
100
80
60
40
20
0
Mar 5
Mar 25
Apr 14
May 4
May 24
Date of outbreak onset


a) 30-days period temperature
Temperature
PM2.5
Population density
Population size
Health exp.
Stringency index
Partial R^2
0.25
0.20
0.15
0.10
0.05
0.00
Mar 5
Mar 25
Apr 14
May 4
May 24
b) Δ14 days period temperature
Partial R^2
0.25
0.20
0.15
0.10
0.05
0.00
Mar 5
Mar 25
Apr 14
May 4
May 24
Date of outbreak onset


a)
Temperature (squared term)
b)
PM2.5
c)
Population density
d)
Population size
e)
Health expenditure
f)
Stringency index
Estimate (95% CI)
Estimate (95% CI)
Mar 5
Mar 25
Apr 14
May 4
May 24
Date of outbreak onset
Date of outbreak onset
Date of outbreak onset


15 March dataset
15 April dataset
15 May dataset
a)
b)
c)
d)
e)
f)
g)
h)
i)
Covid−19 growth rate r
Mean temperature (°C)
PM2.5 (µg/m3)
Stringency index


COVID-19
growth rate
0.05
0.25
0.50
0.72
Importance of candidate drivers
0.25
0.20
0.15
0.10
0.05
0.00
Temperature
PM2.5
Population density
Population size
Health exp.
Stringency index
Mar 5
Mar 25
Apr 14
May 4
May 24
b)
Stringency of containment measures
100
80
60
40
20
0
Mar 5
Mar 25
Apr 14
May 4
May 24
Date of outbreak onset